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Hydroxyapatite Foam as a Catalyst for Formaldehyde Combustion at Room Temperature

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Abstract: The excellent performance of hydroxyapatite, a novel non-precious metal catalyst, for formaldehyde (HCHO) combustion at room temperature is reported. Temperature-programmed surface reaction results indicated that hydroxyl groups bonded with the channel Ca^{2+} may be responsible for adsorption/activation of HCHO.

Formaldehyde (HCHO) is an irritant and carcinogenic volatile organic compound (VOC) released primarily by the degassing of urea−formaldehyde insulation finishing materials; it is also found in particle board and sealants. It is of particular concern in airtight, energy-conserving buildings, as the U.S. Environmental Protection Agency (EPA 600/x-85/362) reports that acute and chronic (long-term, 0.003 ppm) inhalation can lead to eye, nose, and throat inflammation and possibly lung and nasopharyngeal cancer. As a significant segment of the public is exposed to formaldehyde at levels high enough to produce symptoms, an effective means to remove its vapors from closed spaces is of importance.

Combustion of HCHO is presently carried out over precious metal catalysts, such as platinum or palladium.[1−3] It has been found that the concentration of formaldehyde in a two-bedroom house could be reduced from 0.1−0.2 to 0.02−0.05 ppm on a 1 wt % Pd or Pt/Al_2O_3 catalyst at 573 K,[3] while Imamura et al.[4] reported complete conversion of HCHO (900 ppm in air) at the lower temperature of 473 K on a Ru(5 wt %)/CeO_2 catalyst. However, these are expensive procedures due to the high precious metal loading and elevated operating temperatures. In response, a Pt (15 wt %)/SnO_2 catalyst was designed that exhibited high reactivity near room temperature,[5] and most recently, complete combustion was achieved at 360 K over a Mn(18.2 wt %)−Pd(0.44 wt %)/Al_2O_3 co-catalyst in a mixture of 0.53% HCHO and air.[3] Therefore, alternate low-capital-cost and energy-efficient catalytic systems that promote combustion or oxidation of VOCs at room temperature are desirable.

This paper describes a novel alternative where hydroxyapatite (HAp) catalyzes the low-temperature combustion of VOCs without the need to fabricate a metal composite. Hydroxyapatite adopts the ideal composition $Ca_{10}(PO_4)_6(OH)_2$ and possesses a zeolite-like frame that is thermally stable (>1000 K) and contains both acid and base sites, including hydroxyl-enriched channels.[6] The morphology and fine structure of HAp were inspected by scanning electronic microscopy (SEM) and transmission electron microscopy (TEM) (Figure 1). Cation-exchanged and metal-loaded HAp's are versatile catalysts for Diels−Alder and Aldol reactions,[7] aerobic oxidation of alcohols,[8] transformation of ethanol into value-added chemicals,[9] decomposition of hydrogen peroxide,[10] and wet peroxidation of VOCs.[11] Here, we report for the first time the remarkable activity of the phase-pure HAp form as a novel non-precious metal catalyst for the combustion of formaldehyde under ambient conditions.

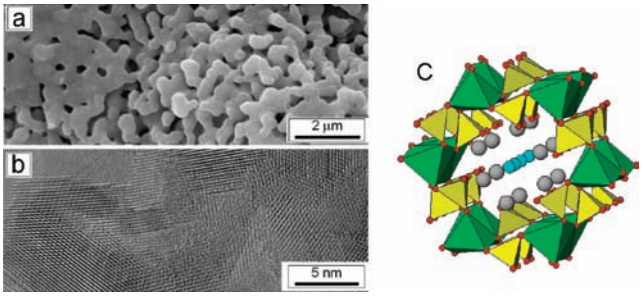

Figure 1. Morphology of HAP: (a) SEM, (b) TEM, and (c) structure drawings of *P*63/*m* $[Ca^{I}_{4}Ca^{II}_{6}](PO_4)_6(OH)_2$ hydroxyapatite. The green polyhedra indicate $Ca^{I}O_6$ metaprisms, the yellow polyhedra indicate PO_4 tetrahedra, gray spheres correspond to Ca^{II}, and blue spheres correspond to OH.

To provide a baseline for comparison, a supported precious metal catalyst, Pd (3 wt %)/γ-Al_2O_3, was measured simultaneously. Details concerning the methodologies employed can be found in the Supporting Information. It was found that at 298 K the conversion of HCHO (X_{HCHO}) was ca. 45% for HAp, only slightly lower than for the Pd catalyst (ca. 57% in Figure 2a). The X_{HCHO} increased steadily with temperature for both catalysts, with 100% conversion achieved at 525 K for HAp and at 475 K for Pd. On the other hand, when ambient conditions were maintained, X_{HCHO} over HAp remained stable at 45% for the first 2 h of reaction but dropped to 28% after running for 10 h, while for the Pd catalyst it declined rapidly from 57% to 33% (Figure 2b). Additionally, the turnover rate is 0.0086 s^{-1} for HAp and 0.006 s^{-1} for the Pd catalyst at 298 K. The methods for calculating the mass-specific and turnover rates are described in Table S1 (Supporting Information).

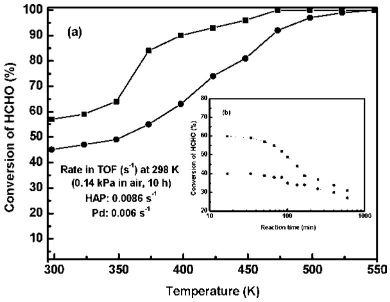

Figure 2. (a) HCHO combustion in the temperature range 298−550 K. (b) HCHO combustion at 298 K for 10 h. Catalysts, (■) Pd (3 wt %)/γ-Al_2O_3 or (●) HAp; feed gas, 0.14 kPa HCHO, 2.6 kPa H_2O in air; GHSV, 36000 h^{-1}. HCHO conversion was calculated on the basis of CO_2 formation.

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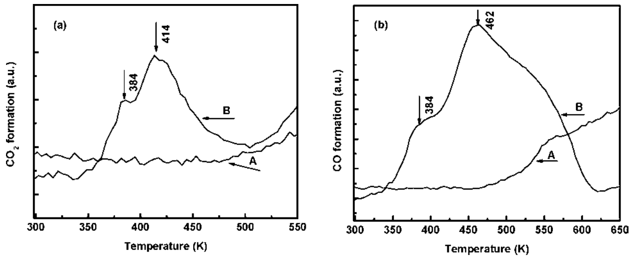

Figure 3. TPSR spectra of (a) CO_2 formation and (b) CO formation obtained from the reaction between HCHO and pre-adsorbed oxygen over (A) HAp and (B) Pd (3 wt %)/γ-Al_2O_3 catalysts.

Clearly, HAp exhibits superior activity and stability toward HCHO combustion under ambient conditions and, to the best of our knowledge, is the first non-precious metal catalyst to demonstrate excellent performance in this reaction system.

To probe the active sites in HAp and study the adsorbed HCHO and its oxidized products during reaction, temperature-programmed surface reaction (TPSR) spectra arising from the interaction between HCHO and pre-adsorbed oxygen were recorded for both catalysts. In the HCHO flow stream, neither CO_2 (curve A in Figure 3a) nor CO (curve A in Figure 3b) was generated over an oxygen-preadsorbed HAp until the temperature was >500 K. In contrast, for the Pd catalyst, CO_2 production occurred at 384 and 414 K (curve B in Figure 3a), and CO appeared at 384 and 462 K (curve B in Figure 3b); similar to HAp, CO_2/CO concentrations rose beyond 500 K.

It can be inferred from these results that (i) the adsorbed oxygen is weakly bonded to HAp and unlikely to be involved in formaldehyde oxidation and/or (ii) the adsorption of oxygen takes place only in the presence of HCHO, as O_2 temperature-programmed desorption spectra from HAp do not contain significant peaks from 298 to 550 K (not shown for brevity). While minor O_2 adsorption on HAp cannot be entirely excluded, it is noted that the dissociative adsorption of oxygen on bare HAp has not been reported. Therefore, it is logical to suppose that the hydroxyl groups located in the HAp channels take part in activating/oxidizing the HCHO molecule, in a catalytic cycle that will be established later.

For the Pd catalyst it is clear that HCHO or its dissociative species react with adsorbed oxygen to produce CO_2 and CO below 500 K. As there are two maxima in the TPSR spectra (Figure 3b), there are at least two distinct active sites on the Pd surface. CO may arise indirectly from partial oxidation of HCHO when limited oxygen is available on the surface or directly as an intermediate during HCHO dissociation. For both catalysts, the enhanced production of CO and CO_2 above 500 K (Figure 3b) can be attributed to the decomposition/disproportionation of HCHO. This conclusion was substantiated by running the same experiment on a reduced Pd surface that only generated CO/CO_2 at high temperature (Figure S3, Supporting Information). Discussion of the surface reactions at elevated temperatures is beyond this study, but it is likely that the pathways for HCHO combustion on the two catalysts are remarkably different.

The diverse functionality of HAp as a catalyst and biocompatible material is achieved, in part, through the limited replacement of Ca^{2+} and P^{5+} by counter-valent ions.[6,8] During room-temperature HCHO combustion on HAp, the hydroxyl groups bonded with the channel Ca^{2+} ($HO\cdots Ca^{2+}$, blue oxyanion in Figure 1c) may act as the active sites, as illustrated in Figure 4. The main steps for this reaction can be concisely described as follows: (i) molecular oxygen first adsorbing on HAp with one O atom bonding to Ca^{2+} and the other O on the C in HCHO; (ii) the two H atoms of HCHO interacting with the two O's that are bound to Ca^{2+} (one from OH and the other from adsorbed dioxygen); and (iii) CO_2 and H_2O produced by simultaneous breaking of Ca−O, O−O, and C−H bonds. While only a small amount of oxygen is perhaps weakly adsorbed through bonding to Ca^{2+}, this may be enhanced in the presence of HCHO due to the formation of O−H bonds, and this may explain why there is almost no HCHO oxidation on HAp during the TPSR experiment in the absence of adsorbed oxygen (Figure 3).

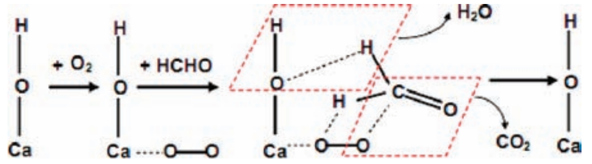

Figure 4. Scheme of HCHO combustion on HAp while hydroxyl groups connected to Ca^{2+} serve as active sites.

In summary, we report for the first time the excellent performance of HAp foam for HCHO combustion under ambient conditions. Preliminary results reveal that hydroxyl groups bonded to Ca^{2+} inside channels of HAp may play an important role in adsorption/activation of HCHO, and a plausible catalytic cycle is proposed to explain the reaction mechanism. Owing to the complexity of this system, more evidence, especially the characterization of HCHO and its intermediates on the HAp surface during reaction, is required. It is suggested that further improvements in activity may be possible by modifying the local environment of the channel Ca---OH groups through partial replacement of Ca^{2+} with other metals such ferric iron ($Ca^{2+} + OH^- \leftrightarrow Fe^{3+} + O^{2-}$) or rare earth elements ($Ca^{2+} + 2P^{5+} \leftrightarrow Ce^{4+} + 2Si^{4+}$; $Ca^{2+} + P^{5+} \leftrightarrow Ce^{3+} + Si^{4+}$) to improve oxygen absorption, and such studies are ongoing. This work gives strong support to the notion that non-precious metal oxide porous ceramics may be designed from inexpensive materials with active sites for promoting low-temperature catalytic combustion of VOCs and other organic pollutants.

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Supporting Information Available: HAp structure, characterization, calculations, and experimental section. This material is available free of charge via the Internet at http://pubs.acs.org.

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